



# Is resistant soil organic matter more sensitive to temperature than the labile organic matter?

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# Is resistant soil organic matter more sensitive to temperature than the labile organic matter?

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## Abstract

A recent paper by Knorr et al. (2005) suggested that the decomposition of resistant soil organic matter is more temperature sensitive than labile organic matter. In Knorr et al.'s model, the reference decay rate was fixed for all pools of soil carbon. We refit Knorr et al.'s model but allow both the activation energy and the reference decay rate to vary among soil C pools. Under these conditions, a similar fit to measured data can be obtained without invoking the assumption that the resistant C pool is more temperature sensitive than the labile pool. Other published evidence does not unequivocally support Knorr et al.'s hypothesis of increased temperature sensitivity of resistant pools of soil carbon.

### 1. Temperature sensitivity of resistant soil organic matter

The response of soil organic carbon (SOC) to temperature change or global warming is important for predicting feedbacks between SOC and climate change. Because of the difficulties and large uncertainties in estimating the temperature sensitivities of the decomposition of soil organic matter (SOM) pools, the relationship between the temperature sensitivity of decomposition and SOM pools is of paramount interest (Townsend et al., 1997; Liski et al., 1999; Ågren, 2000; Giardina and Ryan, 2000; Davidson et al., 2000; Kirschbaum, 2004; Reichstein et al., 2005). Two recent papers highlight current debate in this field. Based on a laboratory incubation of soil samples, Fang et al. (2005) concluded that the decomposition of resistant SOM pool is not less sensitive to temperature than the labile pool. Knorr et al. (2005) used a multi-pool model to fit data from Holland et al. (2000) and suggested that the model can simulate the long-term temperature sensitivity of SOC decomposition, and that the resistant carbon pool is more sensitive to temperature than the labile pool. As the future response of soil stored C to global warming is mainly dependent on the temperature sensitivity of the resistant C pool (Fang et al., 2005), Knorr et al.'s (2005) finding may have important

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implications for future studies. Here, we argue that an assumption used in the model of Knorr et al. (2005) necessarily leads to the conclusion that the resistant pool is more temperature sensitive than the labile pool. We show that if this assumption is incorrect, the finding that resistant C is more sensitive to temperature is not supported.

In Knorr et al. (2005), the decomposition of SOM was simulated with a multiple pool model:

$$\frac{dC_i(t)}{dt} = -k_i C_i(t), \text{ and} \quad (1)$$

$$k_i(T_k) = A \exp(-E_i/RT_k) \quad (2)$$

where  $C_i(t)$  is the  $i$ th carbon pool, decaying at a temperature-dependent rate  $k_i$  over time,  $t$ .  $k_i$  is simulated by the Arrhenius model with the activation energy  $E_i$  varying among C pools and parameter  $A$  (the theoretical decay rate at  $E_i=0$ ) fixed for all pools.  $T_k$  is soil temperature in Kelvin and  $R$  is the universal gas constant (Knorr et al., 2005).

Knorr et al.'s model is similar to many widely used multi-pool models (e.g. Kätterer et al., 1998), but has a new assumption of a fixed " $A$ ". With the assumption of a single  $A$  for all pools, it is implicitly assumed that the slower decomposition in the resistant pools is due only to a higher activation energy,  $E_i$ , and cannot be due to differences in stereochemistry of the decomposing substrats. Differences in stereochemistry would result in a change in the value of  $A$ . The conclusion that the quality difference of SOC pools is due only to the different response of carbon pools to temperature immediately follows from the assumption of fixed  $A$ . This conclusion conflicts with current knowledge about SOM quality and decomposition. We argue that the reference decay rate of decomposition,  $A$ , could be different for each pool. In addition to any differences in activation energy among pools, stereochemical differences between the compounds characterising the resistant pool, and those characterising the labile pool, are likely to influence decomposition. Using Knorr et al.'s (2005) assumption, the resistant carbon pool necessarily has a larger activation energy than the labile pool because of the smaller apparent decomposition rate constant of the resistant pool. A more appropriate

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assumption when fitting the model is that both  $E$  and  $A$  may vary among C pools. The complexity of the model is not increased by allowing both parameters to vary: model complexity is defined by the number of assumptions as well as the number of degrees of freedom, and in our model the assumption of fixed  $A$  is merely replaced by an extra degree of freedom.

By fitting Knorr et al.'s (2005) model to the data from Holland et al. (2000), but allowing both  $A$  and  $E$  to vary among C pools, we show that the fit ( $R^2=0.973$ ) is as good as in Knorr et al. (2005) ( $R^2=0.971$ , Fig. 1a). Fitted parameters ( $c_0=0.071012$ ,  $c_1=1.05556$ ,  $c_2=28.2735$  g C per kg soil,  $E_0=54556$ ,  $E_1=52475$ ,  $E_2=30623$  Jmol $^{-1}$ ,  $A_0=6.1 \times 10^8$ ,  $A_1=9736817$ ,  $A_2=8.09169$ ) do not suggest that the resistant pool is more sensitive than the labile pool. As noted by Knorr et al. (2005), parameters for the third pool are not relevant as this pool is effectively constant over biological timescales. If only allowing  $A$  to change, the goodness-of-fit ( $R^2=0.972$ , fitted  $E=50564$  Jmol $^{-1}$  for all pools) is still similar to that reported in Knorr et al. (2005).

Knorr et al. (2005) (this issue) suspect that allowing both  $A$  and  $E$  to vary among C pools may result in the model becoming self-contradictory due to an initially more labile pool becoming a more stable pool at some cross-over temperature. Such a cross-over is not self-contradictory as the relative decomposition rates of the pools could theoretically change with temperature, depending on the relative importance of activation energy and stereochemistry in mediating decomposition. Furthermore, a cross-over is unlikely to occur. Even with a large activation energy for the resistant pool as assumed in Knorr et al. (2005), changing temperature from  $-10$  to  $50^\circ\text{C}$  will cause a change in the turnover rate of the most resistant pool at a rate about 15 times faster than that of the labile pool ( $E$ -related difference). This difference is smaller than the difference in the value of the reference turnover rate,  $A$ , observed for resistant and labile pools in experiments (Kätterer et al., 1998), and simulated in present models (e.g. the Roth-C model, Coleman and Jenkinson, 1996; the CENTURY model, Parton et al., 1987). In a two-pool model,  $A$  is commonly 100 times larger in the labile pool than in the resistant pool (Kätterer et al., 1998). Allowing both  $A$  and  $E$  to vary is

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unlikely to cause a cross over in decomposition rates of labile and resistant C pools with changing temperature.

We have also fitted the model with the data from our incubation experiment (Fang et al., 2005) by varying  $E$  only, varying both  $A$  and  $E$ , and varying  $A$  only. The fit is almost the same for the three different scenarios (Fig. 1b), and does not show that the decomposition of resistant C pool is more sensitive than the labile pool under combinations of fixed/variable  $E$  and  $A$ . We contend that fitting the model to available data is not a sensitive way to determine whether soil C pools respond differently to temperature variation. A good fit between measured and modelled data does not necessarily imply that all model assumptions are correct. We feel that it is more appropriate in a model such as that used in Knorr et al. (2005) to allow both  $A$  and  $E$  to vary. When this is done, fitting the model to either the original data, or that of Fang et al. (2005), suggests that resistant C is not more sensitive to temperature than labile C.

Knorr et al. (2005) used data of 13 incubated samples compiled in Kätterer et al. (1998) as further evidence that resistant organic matter is more temperature sensitive than the labile pool. A significant negative correlation ( $R^2=0.49$ ) between the activation energy and the initial fraction of the labile pool was taken as evidence that the resistant pool is more temperature sensitive than the labile pool. The 13 samples can be divided into two groups: soil or amended soil (9 samples from five experiments) and plant material (4 samples from other two experiments). The significant correlation referred to in Knorr et al. (2005) is due a significant difference between the two groups (Fig. 2). There is no clear correlation within each group ( $R^2=0.06$  and  $0.29$  for soil and plant material, respectively). The apparent significant correlation between activation energy and the aggregated turnover time in Kätterer et al. (1998), as stated by Knorr et al. (2005) largely depends on the three samples of plant material from a single study conducted by Waksman and Gerretsen (1931) and appears to be an artefact of combining different groups of data. Furthermore, the aggregated turnover time by Knorr et al. (2005) for the data in Kätterer et al. (1998) from different sites was not solely related to the quality of organic matter (or to the fractions of resistant and labile pools), as other

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conditions, e.g. the microbial community, also changed with sites.

2. Other evidence for higher temperature sensitivity of resistant SOM?

Warming soils in controlled experiments is used as an analogue of global warming. With a prolonged warming experiment, warming effects on SOM decomposition have been shown to decline with time (Luo et al., 2001; Rustad et al., 2001; Ström-gren, 2001). This decline was previously explained as the increase in the proportion of resistant pool at later stages with the resistant pool being less sensitive to warming (Peterjohn et al., 1994), or as an adaptation of the microbial community to enhanced temperature (Luo et al., 2001; Ström-gren, 2001). Other recently published work, however, suggests that a reduced turnover rate of SOM to increased soil temperature over time is due to depletion of readily decomposable substrate (Kirschbaum, 2004; Elias-son et al., 2005). These papers suggest that the fractional change of C pools can account for the change in respiration rate over time, though the temperature sensitivity for decomposition remains unchanged. The findings are consistent with data from soil warming experiments and do not need to invoke a different temperature sensitivity of labile and resistant SOC to explain observed results.

It has been suggested that low quality organic matter (equivalent to more resistant SOM pools) is more temperature sensitive, based on the assumed thermodynamics of enzyme kinetics (Bosatta and Ågren, 1999). However, this hypothesis has not been verified by experiment due to the difficulty in partitioning SOM pools and their temperature sensitivities. Some other recent experiments also suggest that the decomposition of resistant C components may be more sensitive to temperature change (Fierer et al., 2003; Fierer et al., 2005). In these experiments, soil respiration rate was determined by the change in headspace CO<sub>2</sub> concentration over 24 h. At the end of the period, the headspace CO<sub>2</sub> concentration with the organic matter (OM) of high quality and at high temperature (up to 2% of the air in headspace) was significantly higher than that with low quality OM at low temperature (a few hundred parts per million). The respiration

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rate in some of the samples (high quality, at high temperature) could have been inhibited by the high headspace concentration of CO<sub>2</sub> (Qi et al., 1994). The possibility that the Q<sub>10</sub> value for high quality OM (or labile pool) has been underestimated cannot be eliminated from these experiments.

### 3. Conclusions

Because there are stereochemical reasons why the reference decay rate, *A*, can vary between pools, and we have shown that if *A* is allowed to vary, the resistant pool is not necessarily more sensitive to temperature than the labile pool, we feel that the conclusion of Knorr et al. (2005) that resistant SOC is more sensitive to temperature than labile SOC, is unsafe. Whilst we do not exclude this possibility, we do not feel that published evidence unequivocally supports this hypothesis. Further study is clearly merited.

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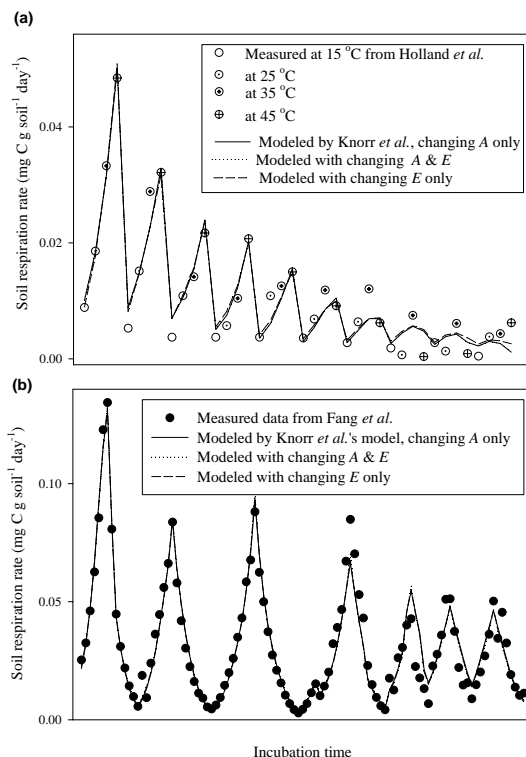
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**Fig. 1.** Comparison between modelled and measured data among models. Measured data are average of all samples. **(a).** Data from Holland *et al.* (2000) cited by Knorr *et al.* (2005). Soil samples were taken from a tropical forest in Brazil, and were incubated for 24 weeks under different constant temperatures (15, 25, 35, and 45 °C). Sample size was 10–15 g. **(b).** Measured respiration rate from Fang *et al.* (2005) for soils under a middle-aged plantation of Sitka spruce in Scotland. Soil samples (4 samples with 4 replicates, each weighed 600–800 g) were incubated for 102 days under changing temperature (4–44 °C, with a step of 4 °C).

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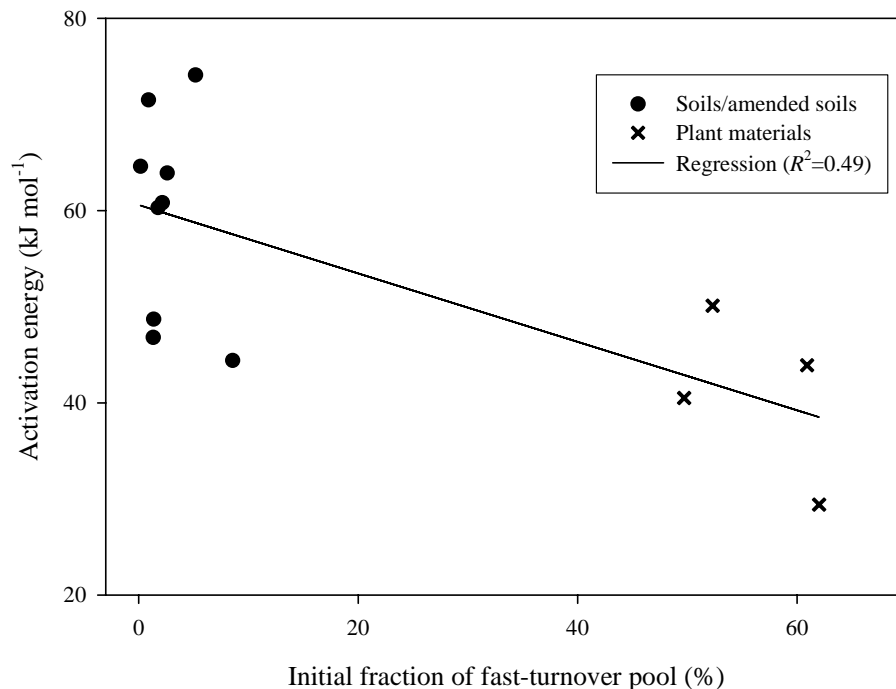
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**Fig. 2.** The relationship between the activation energy and the initial fraction of the fast-turnover pool for the data referred to by Knorr et al. (2005). A two-pool model, similar to Eqs. (1) and (2), was fitted to observed data but the activation energy was assumed to be the same for both pools (Kätterer et al., 1998).

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